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**ROCKETDYNE**

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION  
6633 CANOGA AVENUE, CANOGA PARK, CALIFORNIA 91304

R-7239-2

(Unclassified Title)

QUARTERLY PROGRESS REPORT,  
INORGANIC HALOGEN OXIDIZERS

(1 September 1967 through 30 November 1967)

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**PREPARED BY**

D. Pilipovich  
C. J. Schack  
K. O. Christe  
R. D. Wilson

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**APPROVED BY**

*E. A. Lawton*

E. A. Lawton  
Manager

Synthetic and Propellant Chemistry  
Research Division

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## FOREWORD

The research reported herein was performed by members of the technical staff of the Rocket-dyne Research Division and was supported by the Office of Naval Research, Power Branch Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Navy Contract Nonr 4428(00) and covers the period 1 September 1967 through 30 November 1967.

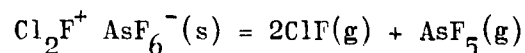
The program manager was Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The work was conducted in Oxidizer and Fluorine Chemistry with Dr. D. Pilipovich, Principal Scientist as project scientist. Full-time staff members contributing to the technical effort were Dr. C. J. Schack, Dr. K. O. Christe, and Mr. R. D. Wilson.

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## ABSTRACT

Ultraviolet activated fluorinations of chlorine oxyfluorides at low temperatures to produce Florox were continued. Experiments were designed to corroborate the previously proposed mechanism of the reaction. Results were obtained that were incompatible with those predicted from the postulate. The involvement of elemental  $\text{Cl}_2$  and  $\text{O}_2$  in the Florox forming process was deduced and was verified experimentally by the preparation of Florox from  $\text{Cl}_2$ ,  $\text{F}_2$ , and  $\text{O}_2$ . Additional reaction paths are proposed and have been partially substantiated.

The chlorofluoro chloronium (III) cation,  $\text{Cl}_2\text{F}^+$ , a new oxidizing species, has been prepared in the form of its  $\text{AsF}_6^-$  and  $\text{BF}_4^-$  salts. The white crystalline  $\text{Cl}_2\text{FAsF}_6$  complex is stable at  $-78^\circ\text{C}$  and is completely dissociated in the gas phase at  $25^\circ\text{C}$ . A pressure-temperature curve gives a heat of reaction of  $32.83 \text{ kcal mole}^{-1}$  for the dissociation process:



Low-temperature infrared measurements on both salts prove the ionic nature of the solids and indicate that  $\text{Cl}_2\text{F}^+$  has a bent structure (symmetry  $\text{C}_s$ ) with chlorine as the central atom. The  $\text{Cl}_2\text{F}^+$  cation is the first example of a catenated polyhalogen cation. Quantitative displacement of 2 ClF from the complex by 1  $\text{FNO}_2$  has been observed.

The synthesis of chlorine perchlorate from ClF and perchlorate species was unsuccessful. Only mixtures of chlorine oxyfluorides and chlorine oxides, including  $\text{Cl}_2\text{O}_6$ , were produced by these reactions. The utility of ClF as a chlorofluorinating agent was demonstrated in the preparation of some new covalent hypochlorites,  $\text{R}_f\text{OCl}$ . These syntheses are catalyzed by alkali metal fluorides but may also be affected by reaction of preformed complexes. Preliminary characterization of hypochlorites has been carried out.

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High-purity bromine nitrate has been prepared by the reaction of  $\text{Br}_2$ ,  $\text{Cl}_2$ , and  $\text{ClNO}_2$  at -30 to 0 C. Solid  $\text{BrNO}_2$  is pale yellow and melts to a golden colored liquid at -31 C. The vapor pressure-temperature equation for -25 to 10 C is  $\log p_{\text{mm}} = 9.6905 - 2254.5/T$ . Fluorination of  $\text{BrNO}_2$  has shown that  $\text{FNO}_2$  and  $\text{BrF}_5$  are the principal products (95+ percent yield). Limited amounts of a white solid  $\text{NO}_2^+$ -bromine fluoride complex are also formed. Partial analysis of this complex indicates no oxygen is present in the anion.

(Confidential Abstract)

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## INTRODUCTION

This program is concerned with the synthesis of new halogen fluorides and oxyfluorides. To achieve this goal, a variety of techniques have been employed in the synthesis of intermediates and their conversion to new fluorides. Of particular recent interest is the use of ultraviolet irradiation as an activating agent on the interaction of chlorine-fluorine-oxygen containing materials. Previous efforts in this area have resulted in the preparation of Florox ( $\text{ClF}_3\text{O}$ ) from  $\text{FClO}_2$  and  $\text{FClO}_3$ . A more detailed analysis of the processes involved in these syntheses has been undertaken. This has been directed toward the verification of a proposed mechanism through correlation of predicted and experimental results. However, discrepancies have been found which indicate that a considerably more complex path is involved than that originally considered.

The chemistry and synthetic utility of  $\text{ClF}$  has been of continuing interest. One aspect of this is the nature of the  $\text{ClF}$ -Lewis acid complexes. A literature report has indicated such complexes to be of 1:1 stoichiometry and earlier work under this contract had indicated that a 3:1  $\text{ClF}$ -Lewis acid reaction occurred. Definitive results were sought therefore, both as to the stoichiometry of the interaction and also the nature of the resultant complex ions. In addition to the ionic derivatives of  $\text{ClF}$ , other reactions have been discovered in which the use of  $\text{ClF}$  has led to synthetic routes to useful covalent materials. Thus, superior syntheses of  $\text{ClNF}_2$ ,  $\text{ClNO}_3$ , and  $\text{PF}_4\text{Cl}$  were developed. Further application of  $\text{ClF}$  has now resulted in the preparation of some new perfluorohypochlorites.

The proven reaction of  $\text{ClNO}_3$  and  $\text{F}_2$  as a route to Florox promoted consideration of a similar  $\text{BrNO}_3$  fluorination as a method of forming the unknown  $\text{BrF}_x\text{O}$  species. The availability of only impure  $\text{BrNO}_3$  was an experimental difficulty encountered previously. However, fluorination of that material indicated that a new  $\text{NO}_2^+$  bromine fluoride complex was formed, possibly  $\text{NO}_2^+\text{BrF}_x\text{O}^-$ . The synthesis of pure  $\text{BrNO}_3$  has now been carried out and its fluorination has been studied.

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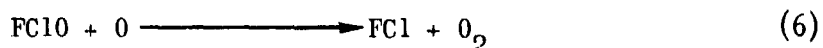
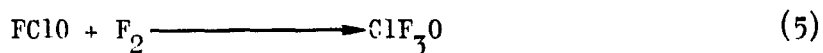
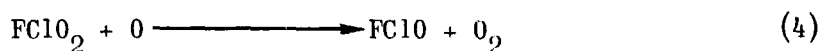
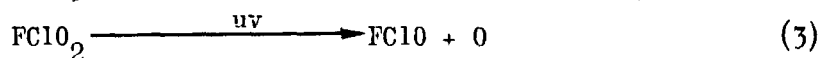
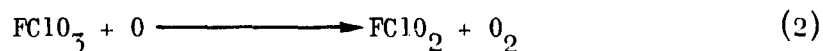
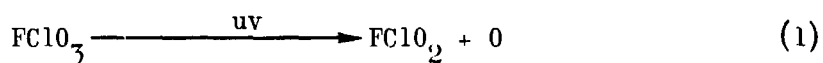
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## DISCUSSION

### ULTRAVIOLET ACTIVATED REACTIONS

The preparation of  $\text{ClF}_3\text{O}$  from any vigorous fluorinating agent and an oxychlorine fluoride ( $\text{FClO}_2$  or  $\text{FClO}_3$ ) was demonstrated to be facile with uv radiation (Ref. 1). These routes were the first demonstrations of high-yield syntheses of  $\text{ClF}_3\text{O}$  not involving inorganic hypochlorites as intermediates. In the previous quarter, it was demonstrated that a marked improvement could be realized in the uv synthesis of  $\text{ClF}_3\text{O}$  by utilizing a more powerful uv source. The early work was accomplished using a 100-watt high-pressure mercury source and the improvements resulted when a 450-watt source was used.

During the past quarter, more attention was directed toward determining possible intermediate reactions in order to unscramble the sequence of processes occurring. Initial reactions utilized the  $\text{F}_2$ - $\text{FClO}_3$  system and are summarized in Table 1. Several features of the uv reaction are noteworthy and inexplicable (at least within the constraints of the working model of the mechanism). A stepwise decomposition of  $\text{FClO}_3$  was suggested in Ref. 2:



The stepwise degradation of  $\text{FClO}_2$  or  $\text{FClO}_3$  seemed reasonable and offered a variety of choices in experimental confirmation.

An examination of the preceding sequence enables several valid predictions to be made concerning the outcome of an experiment. For example, at constant pressure and temperature, the decomposition of  $\text{FClO}_2$  should be a

TABLE 1  
ULTRAVIOLET ACTIVATED REACTIONS

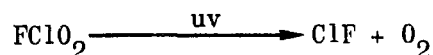
Reaction Number	Reactants	Reactant Ratio, $F_2/FClO_3$	Temperature, °C	Time, * hours	Condensable Products	Percent Conversion	Percent Yield $ClF_3O$
1	$FClO_3$	---	-60	1/2	Unreacted $FClO_3$ , $ClF$ , small amount $FClO_2$ [percent of product = (74%) (23.5%) (2.5%)]	32	
2	$FClO_3$	---	-60	1/2	Unreacted $FClO_3$ , $ClF$ , small amount $FClO_2$ [percent of product = (68.5%) (28%) (3.5%)]	26	
3	$F_2$ , $FClO_3$	1.1	-60	1	$ClF_3O$ , $ClF_3$ , unreacted $FClO_3$ , small amount $FClO_2$	30	60
4	$F_2$ , $FClO_3$	1.2	-60	1/2	$ClF_3O$ , $ClF_3$ , unreacted $FClO_3$ , small amount $FClO_2$	12	33
5	$F_2$ , $FClO_3$	2.0	-60	1	$ClF_3O$ , $ClF_3$ , unreacted $FClO_3$ , small amount $FClO_2$	27	41
6	$F_2$ , $FClO_3$	1.0	-60	1/2	$ClF_3O$ , $ClF_3$ , reacted $FClO_3$ , small amount $FClO_2$	17	46
7	$F_2$ , $FClO_3$	1.0	-60	1 1/2	$ClF_3O$ , $ClF_3$ , unreacted $FClO_3$ , small amount $FClO_2$	40	51
8	$ClF$ , $O_2$	1.0	-60	1	Unreacted $ClF$ , small amounts $ClF_3$ , $FClO_2$ , $Cl_2$	--	--
9	$ClF_3O$	---	-60	1	Unreacted $ClF_3O$ (92%), small amounts $ClF_3$ , $FClO_2$	--	--
10	$ClF_3O$	---	-60	1/2	Unreacted $ClF_3O$ (90%), small amounts $ClF_3$ , $FClO_2$ , $Cl_2$	--	--
11	$ClF_3O$	---	-40	1	Unreacted $ClF_3O$ (72%), small amount $ClF_3$	--	--
12	$ClF$ , $O_2$ , $FClO_3$	1:1:1	-60	1	Unreacted $ClF$ and $FClO_3$ , small amounts of $ClF_3$ and $ClF_3O$ , $Cl_2$	--	--
13	$O_2$ , $FClO_3$	1.0	-60	1	Unreacted $FClO_3$ , $ClF$ , small amounts of $FClO_2$ and $Cl_2$	--	--

\*All reaction periods do not include a 10-minute lamp warm-up period.

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function of time, i.e., longer radiation periods would result in a greater proportion of  $\text{FClO}_3$  decomposition. This was verified experimentally both in the presence and absence of  $\text{F}_2$ .

However, other results expected as a consequence of the proposed scheme were not observed. The overall equation for the decomposition of  $\text{FClO}_2$  is:



Thus,  $\text{FClO}_3$ , when irradiated alone, should yield lower relative concentrations of  $\text{FClO}_2$  (i.e., lower  $\text{FClO}_2/\text{ClF}$  ratios) at longer reaction times. This was not the case, however, since ratios of 1:6 and 1:10 were found at 2- and 1/2-hour irradiation times, respectively. The result was unexpected because  $\text{FClO}_2$ , a stronger absorber in the uv than  $\text{FClO}_3$ , would be expected to decompose at a more rapid rate than  $\text{FClO}_3$  itself.

Considering the postulated reaction sequence, it should be possible to rationalize yield data on  $\text{ClF}_3\text{O}$  formation as a function of time. The average yield of 1/2-hour irradiations was 40 percent compared to an average greater than 50 percent for runs of 1 hour and more. From the proposed scheme, the yield of  $\text{ClF}_3\text{O}$  should be a function of  $\text{FClO}_3$  conversion only and certainly should be constant with respect of time. (Actually, since  $\text{ClF}_3\text{O}$  is decomposed by uv, the yield should decrease somewhat with longer reaction time). Although there is scatter in the results, there is no doubt that the experiments at 1/2 hour led to lower yields of  $\text{ClF}_3\text{O}$  and not the highest yields.

The concentration of  $\text{F}_2$  also seems to strongly affect the yield of  $\text{ClF}_3\text{O}$ . If  $\text{FClO}$  is formed and fluorinated as in Eq. 5, it is not unreasonable to expect that a higher relative concentration of fluorinating agent should favor a higher yield of  $\text{ClF}_3\text{O}$ . The results in Table 1 and in Ref. 2 are

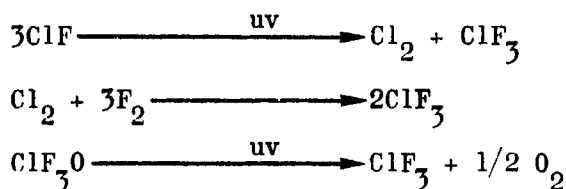
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both contrary to this postulate. The enhanced absorbancy of  $F_2$  or  $ClF_5$  coupled with the high partial pressure may affect the conversion of  $FClO_3$  but certainly should not lower the yield of  $ClF_3O$ .

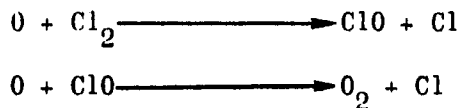
Since the results are not consistent with the postulated reaction sequence, experiments were conducted to determine the effect of the decomposition products of  $FClO_3$  on the reactants and on the intermediates. Irradiating  $ClF$  and  $O_2$  did not indicate the fixation of  $O_2$  but did show the disproportionation of  $ClF$ :



Chlorine was also a product of the  $ClF-O_2-FClO_3$  and  $O_2-FClO_3$  systems. The  $ClF_3$  which was always formed along with  $ClF_3O$  may have arisen from several reactions, namely:



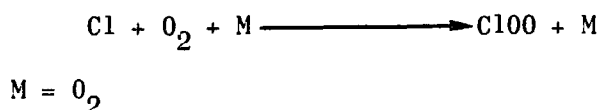
Since  $Cl_2$  is formed in these reactions and easily dissociated in the uv, the possibility existed that  $Cl_2$  may participate in the actual formation of  $ClF_3O$ . The catalytic effect of  $Cl_2$  in the recombination of atomic oxygen has been recognized (Ref. 3), and was thought to involve a  $ClO$  radical intermediate:



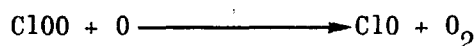
Recently, the postulate of the  $ClO$  radical being formed was proved in studying the reaction of atomic oxygen and  $Cl_2$  (Ref. 4). Thus, the fixation of the intermediate  $ClO$  radical in the  $FClO_x - F_2$  system may be promoted by the use of  $Cl_2$ .

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The formation of ClO radicals in the flash photolysis of Cl<sub>2</sub> and O<sub>2</sub> led Benson and Buss (Ref. 5) to suggest that the rate-controlling step in the recombination catalysis is the termolecular reaction:

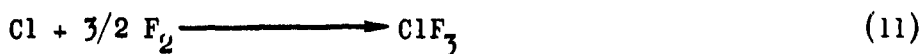
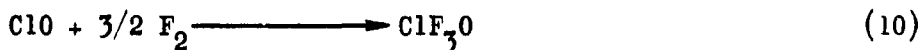
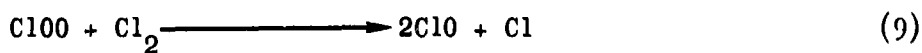
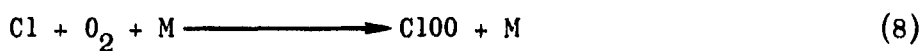
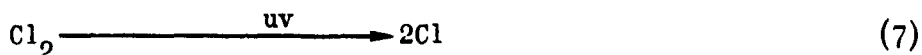


with a subsequent decomposition to ClO:



This postulate suggested that the ClO moiety may be trapped with F<sub>2</sub> in an experiment with an activated mixture of F<sub>2</sub>, Cl<sub>2</sub>, and O<sub>2</sub>. The first attempt under this program to "fix" the ClO radical postulated to form as above was successful inasmuch as a 16 percent yield of ClF<sub>3</sub>O was obtained (Table 2, Reaction 1). As is evident, the Cl<sub>2</sub> and F<sub>2</sub> were introduced into the cell in a stoichiometric amount with O<sub>2</sub> being in excess. A material balance exceeding 98 percent was realized with all of the Cl<sub>2</sub> being reacted.

The reproducible formation of ClF<sub>3</sub>O from the elements offered additional latitude in exploring the possible intermediates responsible for ClF<sub>3</sub>O formation in the uv reaction. The fact that more than 80 percent of the lamp output was at wavelengths longer than 3000 angstroms coupled with the facile reaction observed suggested that Cl<sub>2</sub> was the principal species being activated and that the termolecular reaction proposed by Benson and Buss may well be occurring in the Cl<sub>2</sub>-F<sub>2</sub>-O<sub>2</sub> system. Certainly some F<sub>2</sub> activation should occur but little or no O<sub>2</sub> activation is possible with the lamp used. For example:



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TABLE 2  
ULTRAVIOLET ACTIVATED REACTIONS USING  $\text{Cl}_2$ ,  $\text{F}_2$ , AND  $\text{O}_2$

Reaction Number	Mole Ratio $\text{Cl}_2:\text{F}_2:\text{O}_2$	Temperature, C	Time, hours	Condensable Products	Percent Yield $\text{ClF}_3\text{O}$
1	1:3:10	-60	1*	$\text{ClF}_3\text{O}$ , $\text{ClF}_3$	16
2	1:3:10	-60	1*	$\text{ClF}_3\text{O}$ , $\text{ClF}_3$	16
3	1:3:1	-60	1*	$\text{ClF}_3$ , trace amounts $\text{ClF}_3\text{O}$ , $\text{ClF}_5$	Trace
4	1:3.3:18.7	-60	1**	$\text{ClF}_3\text{O}$ , $\text{ClF}_3$ , trace amount $\text{FClO}_2$	8
5	1:1.1:11.5	-60	1**	$\text{ClF}_3\text{O}$ , $\text{ClF}_3$ , $\text{ClF}$ , trace amount $\text{FClO}_2$ , possibly small amount of unreacted $\text{Cl}_2$	2 to 3
6	1:3.5:10.7	-60	1/4**	$\text{ClF}_3$ , trace $\text{ClF}_3\text{O}$	Trace
7	1:3.4:9	-60	2**	$\text{ClF}_3\text{O}$ , $\text{ClF}_3$ , trace $\text{ClF}_5$	18
8	1:3.2:10	-60	1/4**	$\text{ClF}_3$ , trace amounts of $\text{ClF}_5$ , $\text{ClF}_3\text{O}$ (Note: poor $\text{Cl}_2$ balance in experiment)	Trace
9	1:3.5:10	-60	1/4**	$\text{ClF}_3$ , trace amount of $\text{ClF}_3\text{O}$	Trace
10	1:3.3:10	-60	1/2**	$\text{ClF}_3$ , $\text{ClF}_3\text{O}$ , small amounts of $\text{FClO}_2$ , $\text{ClF}_5$	2
11	1:3:10	-60	1/6**	$\text{ClF}$ , $\text{ClF}_3$ , small amount $\text{FClO}_2$ , possibly some unreacted $\text{Cl}_2$	0
12	1:3.2:10	-60	1/12**	$\text{ClF}$ , $\text{ClF}_3$ , small amount $\text{FClO}_2$ , possibly some unreacted $\text{Cl}_2$	0
13	1:3.2:10	-40	1**	$\text{ClF}$ , small amount $\text{FClO}_2$ , possibly $\text{Cl}_2$	***
14	1:3.3:10	-40	1**	$\text{ClF}_3\text{O}$ , $\text{ClF}_3$ , $\text{ClF}$ , small amount $\text{FClO}_2$	5

\*Reaction periods do not include a 10-minute lamp warm-up period.

\*\*Apparatus was modified to include a window shade which is employed during lamp warm up; periods indicated are actual time reactants exposed to uv irradiation.

\*\*\*Validity of experiment in question due to the small amount of fluorine-containing product recovered.

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From the preceding sequence, it is apparent that Eq. 11 may function as both the termination step and competing step (formation of  $\text{ClF}_3$ ).

The sequence (Eq. 7 through 11) is supported by several considerations of known reactant systems but also appears to fall short of predictions when the time variable is treated. From Table 2 it is seen that essentially no  $\text{ClF}_3\text{O}$  is formed at short reaction times with almost all of the  $\text{Cl}_2$  being consumed to  $\text{ClF}_3$ . (These results could suggest a subsequent  $\text{ClF}_3\text{-O}_2$  reaction). Despite the fact that much basic information has been acquired regarding the operative processes in these uv activated reactions, considerably more experimentation is necessary before a complete clarification of the reaction process is possible.

## CHEMISTRY OF CHLORINE MONOFLUORIDE

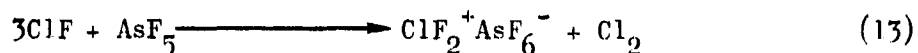
Reactions of chlorine monofluoride have been the subject of continuing investigations under this program. This work has proved successful from both a synthetic viewpoint and also in elucidating basic modes of reaction of interhalogen fluorides. During this period, this work has been carried on in several areas.

### Chlorine Monofluoride--Lewis Acid Systems

Previous work on the  $\text{ClF}$ -Lewis acid system is controversial. Schmeisser (Ref. 6) reported the formation of solid complexes containing the  $\text{Cl}^+$  cation according to the following equation:



Earlier results from this laboratory (Ref. 1) seemed to indicate a disproportionation of  $\text{ClF}$  according to the following equation:



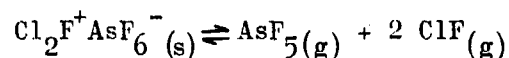
Determination of the combining ratio between  $\text{ClF}$  and  $\text{AsF}_5$  would allow a clearcut choice between Eq. 12 and 13. Quantitative synthesis of the

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solid complex from either excess ClF or excess AsF<sub>5</sub> resulted in a 1.00:2.02 and 1.09:2.00 combining ratio, respectively, thus proving that neither Eq. 12 nor 13 occurs. The resulting white, crystalline solid is stable at -78 C and is completely dissociated (according to its infrared spectrum) into AsF<sub>5</sub> (g) + 2 ClF (g) at ambient temperature. These infrared data further support the observed 1:2 combining ratio. The vapor pressure-temperature relation was measured and a plot of log p<sub>(mm)</sub> vs 1/T resulted in a straight line, which can be expressed by the equation:

$$\log p_{(\text{mm})} = 11.7124 - \frac{2391.6}{T}$$

By extrapolation, a dissociation pressure of 1 atmosphere was obtained at -2.4 C. At 25 C, the dissociation pressure amounts to 4864 millimeters. From the slope of the vapor pressure-temperature curve, a heat of reaction ( $\Delta H$ ) of 32.83 kcal/mole was calculated from the process:

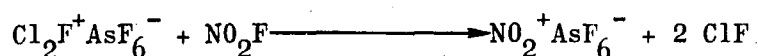


From  $\Delta F_T^\circ = -RT \ln K_p (\text{atm})$ , a free energy change,  $\Delta F_{298}^\circ = -2.16$  kcal/mole, and from  $\Delta S_T^\circ = (\Delta H^\circ - \Delta F_T^\circ)T^{-1}$ , an entropy change,  $\Delta S_{298}^\circ = 117.41$  cal deg<sup>-1</sup> mole<sup>-1</sup> were found for the dissociation process at 25 C. A heat of formation of  $\text{Cl}_2\text{F}^+\text{AsF}_6^-(\text{s})$ ,  $\Delta H_{f298}^\circ = -355.4$  kcal mole<sup>-1</sup>, was calculated based upon  $\Delta H_{f298}^\circ$  of  $\text{ClF}(\text{g}) = 13.5$  kcal mole<sup>-1</sup> (Ref. 7) and  $\Delta H_{f298}^\circ$  of  $\text{AsF}_5(\text{g}) = 295.6$  kcal mole<sup>-1</sup> (Ref. 8).

The fact that the dissociation pressure-temperature curve is a straight line over the entire temperature range measured and that at all temperatures only ClF and AsF<sub>5</sub> gas in a 2:1 mole ratio (according to their infrared spectra) were given off, shows that no stepwise decomposition (including the formation of stable intermediates such as  $\text{Cl}^+\text{AsF}_6^-$ ) occurs. Thus, it seems that the  $\text{Cl}^+\text{AsF}_6^-$  complex reported by Schmeisser, does not even form as an intermediate and that Schmeisser most probably mistook the  $2 \text{ClF} \cdot \text{AsF}_5$  complex for  $\text{Cl}^+\text{AsF}_6^-$ . Elemental analysis of a sample of the complex (after hydrolysis in aqueous NaOH solution) showed an As to Cl mole ratio of 1.0:1.8, in agreement with a 1:2 and not a 1:3 or a 1:1 combining ratio.

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Nitryl fluoride, when allowed to react with excess solid  $2\text{ClF}\cdot\text{AsF}_5$ , displaced ClF in a mole ratio of  $\text{NO}_2\text{F}:\text{ClF} = 1.00:1.94$ . The infrared spectrum of the solid residue showed after removal of all the excess  $2\text{ClF}\cdot\text{AsF}_5$  (by pumping at ambient temperature) the following bands characteristic of  $\text{NO}_2^+\text{AsF}_6^-$  (Ref. 9 and 10); 2360 m ( $\nu_{\text{as}} \text{NO}_2^+$ ), 695 vs ( $\nu_{\text{as}} \text{AsF}_6^-$ ) 601 m ( $\delta \text{NO}_2^+$ ), and 402 m ( $\delta_{\text{as}} \text{AsF}_6^-$ ). Hence, the following reaction took place:



The ionic nature of the  $2\text{ClF}\cdot\text{AsF}_5$  adduct has been proven by its low-temperature infrared spectrum taken on an Infracord 337 (refer to Fig. 1). The observed frequencies are listed in Table 3 and their assignment will be subsequently discussed.

Investigation of the  $\text{ClF}\cdot\text{BF}_3$  system shows that again the complex  $\text{Cl}^+\text{BF}_4^-$ , reported by Schmeisser (Ref. 6), does not form. Quantitative synthesis, using an excess of ClF, resulted in a  $\text{BF}_3$  to ClF combining ratio of 1.00:2.03. The white crystalline solid obtained is stable at  $-127^\circ\text{C}$ . At  $-112^\circ\text{C}$ , it shows a measureable dissociation pressure. Attempts to obtain a dissociation pressure-temperature curve failed owing to difficulties in attaining equilibrium. Under the experimental conditions used, the recombining speed of ClF and  $\text{BF}_3$  appeared to be extremely slow. The  $2\text{ClF}\cdot\text{BF}_3$  complex is considerably less stable than the corresponding  $\text{AsF}_5$  adduct. This is not surprising because  $\text{BF}_3$  when compared to  $\text{AsF}_5$ , is known to act as a weaker Lewis acid towards halogen fluorides (Ref. 11).

The ionic nature,  $\text{Cl}_2\text{F}^+\text{BF}_4^-$ , of the adduct has also been proven by its low-temperature infrared spectrum (Fig. 2). The observed frequencies and their assignments are listed in Table 3.

Several structural possibilities exist for 2:1 adducts of ClF with Lewis acids. The complexes could be either fluorine-bridged coordination complexes or ionic complexes containing the  $\text{Cl}_2\text{F}^+$  cation. The first possibility can be definitely ruled out by comparison of the data of Table 3

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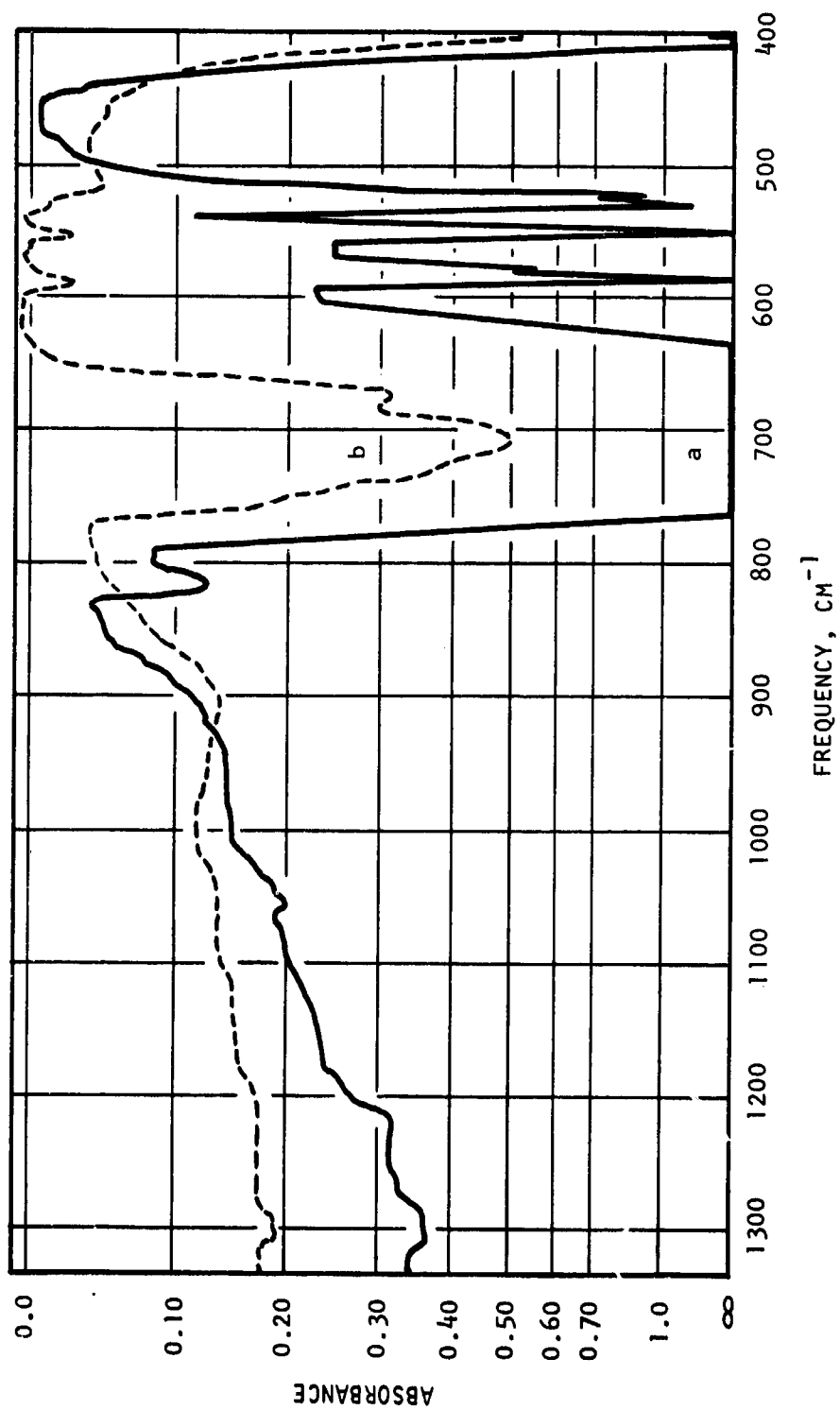


Figure 1. Low-Temperature Infrared Spectrum of Solid  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  at Two Different Concentrations

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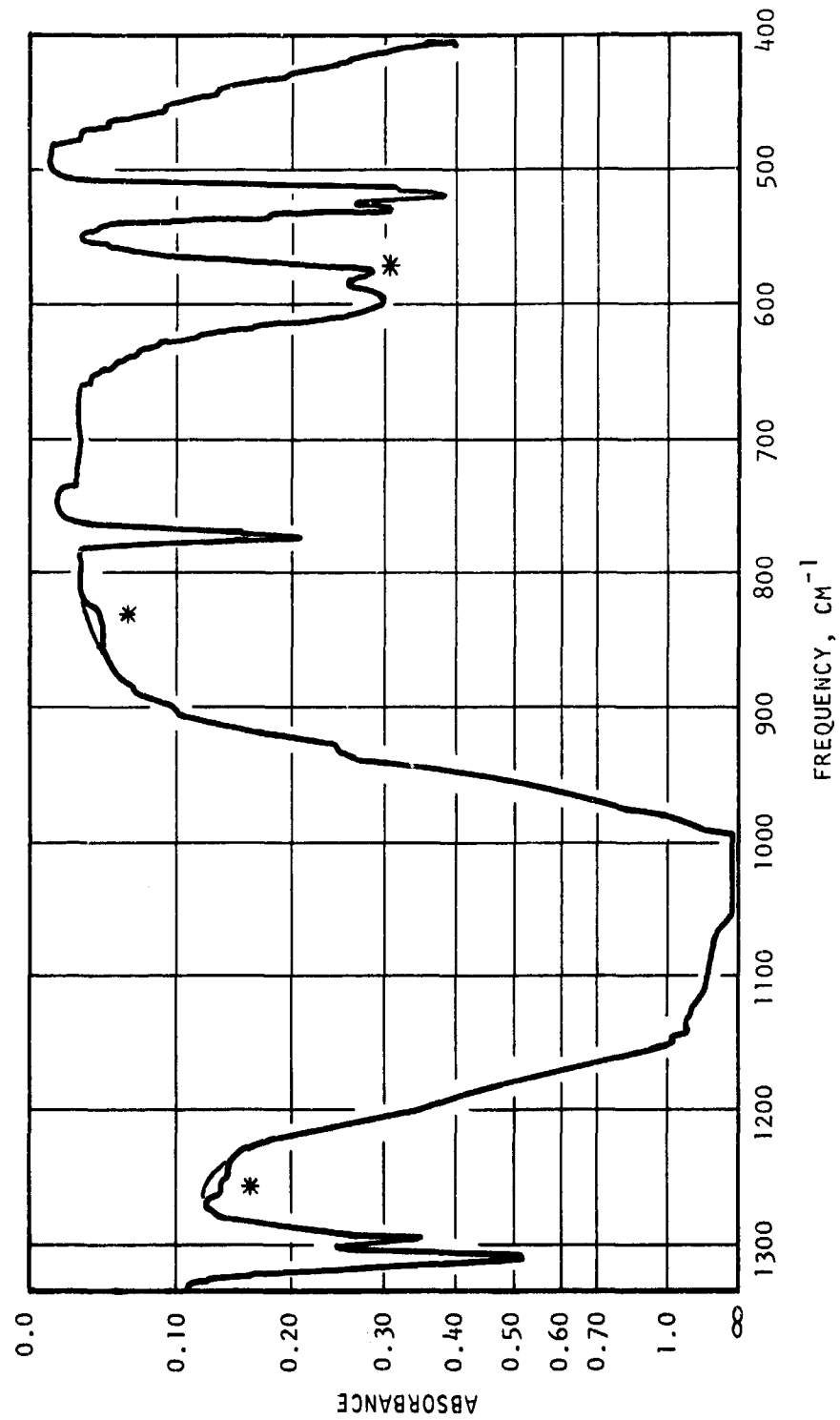


Figure 2. Low-Temperature Infrared Spectrum of Solid  $\text{Cl}_2\text{F}^+\text{BF}_4^-$ .  
(The bands marked by an asterisk are due to solid  $\text{ClO}_2\text{F}$ .)

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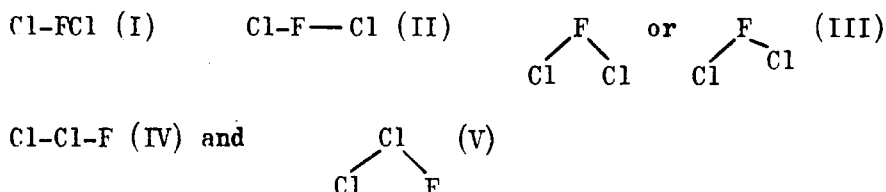
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TABLE 3

INFRARED SPECTRA OF  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  AND  $\text{Cl}_2\text{F}^+\text{BF}_4^-$  AS SOLIDS  
AT  $-196^\circ\text{C}$  AND THEIR ASSIGNMENT

Frequencies Observed, $\text{cm}^{-1}$ , Intensity		Assignment (Pointgroup)		
$\text{Cl}_2\text{F}^+\text{BF}_4^-$	$\text{Cl}_2\text{F}^+\text{AsF}_6^-$	$\text{Cl}_2\text{F}^+(\text{Cs})$	$\text{BF}_4^-(\text{T}_d)$	$\text{AsF}_6^-(\text{O}_h)$
	1312   1297   vw			$(\nu_2 + \nu_3)$
1305 m   1289 mw   1145 - 978 vs, b			$(\nu_1 + \nu_4)$ $\nu_3(\text{F}_2)$	
	828 w			$(\nu_2 + \nu_6)$
766 mw			$\nu_1(\text{A}_1)$	
	703 vs			$\nu_3(\text{F}_{1u})$
590 m	586 m	$\nu_1(\text{A}')\text{Cl}^{35}\text{-F}$		
582 w, sh	578 mw (548 m)	$\nu_1(\text{A}')\text{Cl}^{37}\text{-F}$		
528 mw, sh	529 m	$\nu_3(\text{A}')\text{Cl}^{35}\text{-Cl}^{35}$		
523 mw, sh	521 mw	$\nu_3(\text{A}')\text{Cl}^{37}\text{-Cl}^{35}$		
	514 vw, sh	$\nu_3(\text{A}')\text{Cl}^{37}\text{-Cl}^{37}$		
519 m			$\nu_4(\text{F}_2)\text{B}^{10}$	
512 w, sh			$\nu_4(\text{F}_2)\text{B}^{11}$	
	402 m			$\nu_4(\text{F}_{1u})$

with that reported for similar  $\text{BF}_4^-$  and  $\text{AsF}_6^-$  containing complexes such as  $\text{ClF}_2^+\text{BF}_4^-$  and  $\text{ClF}_2^+\text{AsF}_6^-$ , respectively (Ref. 12). All vibrations characteristic of the  $\text{BF}_4^-$  and  $\text{AsF}_6^-$  anion have been observed with known frequencies and intensities. Therefore, the adducts of  $\text{ClF}$  with Lewis acids are ionic, containing the  $\text{BF}_4^-$  and  $\text{AsF}_6^-$  anion and consequently also the  $\text{Cl}_2\text{F}^+$  cation. This cation could have either fluorine or chlorine as a central atom and could be either bent or linear, centrosymmetric or asymmetric. Thus, the following structures are possible:



All five models should exhibit three fundamental vibrations of which two are stretching and one is a deformation vibration. Model I (belonging to point group  $D_{\infty h}$ ) is the only structure having a symmetry center. Therefore, only one of the stretching vibrations should be infrared active for Model I assuming that the selection rules apply strictly. For models II to V, all three fundamentals are expected to be infrared active. The data of Table 3 (observation of at least two stretching vibrations at approximately  $585$  and  $525 \text{ cm}^{-1}$ , respectively) thus rule out model I. The deformation vibration is expected to occur at a frequency below  $400 \text{ cm}^{-1}$ . This prediction is based on the calculation of the frequency of the deformation mode assuming that the force constants would be identical with those of  $\text{ClF}_2^+$  (Ref. 12) and considering only the increase of mass resulting from the substitution of one fluorine atom by a chlorine atom. The frequency thus obtained is approximately  $390 \text{ cm}^{-1}$ . Because the force constants in  $\text{Cl}_2\text{F}^+$  can be expected to be lower than those in  $\text{ClF}_2^+$ , the actual frequency of the deformation mode should be lower than  $390 \text{ cm}^{-1}$ . Hence, the two bands observed (in addition to the bands characteristic of the anions) most likely represent the two stretching modes of  $\text{Cl}_2\text{F}^+$ .



Distinction between the linear structures (II and IV) and the bent structures (III and V) can be made on the following basis. In a linear X-Y-Z model, very strong coupling should occur between the X-Y and Z-Y stretching vibration, thus resulting in a symmetric and antisymmetric stretching vibration. The latter are expected to be separated by a relatively large frequency difference. In a bent triatomic species however the frequency difference between the two stretching vibrations would be rather small. This prediction was demonstrated previously for linear  $[\text{F}-\text{Cl}-\text{F}]^-$  ( $\nu = 160 \text{ cm}^{-1}$ , Ref. 13) and bent  $[\text{F}-\text{Cl}-\text{F}]^+$  ( $\Delta\nu = 8 \text{ cm}^{-1}$ ) ions (Ref. 12). For a linear  $[\text{Cl}-\text{Cl}-\text{F}]^+$  cation  $\Delta\nu$  should be even larger than for  $\text{ClF}_2^-$  because of the different mass of the two terminal atoms. The frequency difference of approximately  $60 \text{ cm}^{-1}$ , observed for  $\text{Cl}_2\text{F}^+$ , therefore eliminates the possibility of the linear models II and IV.

Distinction between the two remaining bent models (III and V) can be made on the basis of the isotope-splitting observed in the spectrum of  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$ . For model III having only F-Cl bands, only two isotope bands ( $\text{Cl}^{35}\text{-F}$  and  $\text{Cl}^{37}\text{-F}$  in a 3:1 ratio) would be expected for both stretching vibrations. For model V, the higher frequency band (being the Cl-F stretching mode) should show two isotope bands in a 3:1 ratio ( $\text{Cl}^{35}\text{-F}$  and  $\text{Cl}^{37}\text{-F}$ , respectively), whereas the lower frequency band (being the Cl-Cl stretching mode) should show three isotope bands in a 2.2:1.5:0.2 ratio ( $\text{Cl}^{35}\text{-Cl}^{35}$ ,  $\text{Cl}^{37}\text{-Cl}^{35}$  +  $\text{Cl}^{35}\text{-Cl}^{37}$ , and  $\text{Cl}^{37}\text{-Cl}^{37}$ , respectively). Comparison of these predictions with the data of Table 3 and Fig. 1 shows that only model V can be correct.

The fact that the  $\text{Cl}_2\text{F}^+$  cation forms rather than a  $\text{Cl}^+$  cation is not surprising since  $\text{Cl}^+$ , possessing only an electron sextet, should be relatively unstable. By the addition of 1 mole of  $\text{ClF}$  to  $\text{Cl}^+$ , a cation ( $\text{Cl}_2\text{F}^+$ ) results which yields a stable electron configuration for each atom. The  $\text{Cl}_2\text{F}^+$  cation could be considered either as a catenated cation derived from  $\text{Cl}^+$  or as a derivative of  $\text{ClF}_2^+$  in which one of the fluorine ligands has been replaced by a chlorine atom. In the latter case, addition of a fluoride

anion to  $\text{Cl}_2\text{F}^+$  does not result in the parent molecule  $\text{Cl}_2\text{F}_2$  (derived from  $\text{ClF}_3$  by replacement of one F by one Cl atom) but in two molecules of  $\text{ClF}$ . This has been demonstrated by the replacement reactions with  $\text{NO}_2\text{F}$  and the dissociation data obtained for the solid complex.

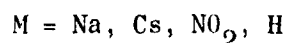
Since  $\text{Cl}_2\text{F}^+$  can be considered as the first known example of a catenated interhalogen cation, its discovery may open a synthetic route to a large number of novel mixed interhalogen compounds.

## Attempted Synthesis of Chlorine Perchlorate

The preparation of the unknown compound chlorine perchlorate was sought to explore its potential as a synthetic intermediate. The synthesis of chlorine perchlorate was attempted via condensation reactions of chlorine monofluoride and various perchlorate species as shown:



where



Condensation reactions of this type have proved useful in syntheses of chlorine nitrate (Ref. 14) and chlorodifluoramine (Ref. 15).

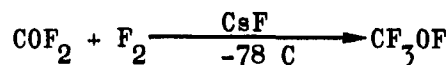
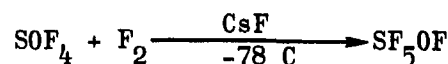
Numerous reactions were conducted with  $\text{ClF}$  and  $\text{NaClO}_4$  or  $\text{CsClO}_4$  using reaction temperatures of  $-78$ ,  $-45$ , and  $0$  C. These reactions were of variable duration of up to 2 weeks. During nearly all experiments, a low yield (0 to 10 percent) of a volatile Cl-O species was obtained. The identity of this compound as a perchlorate was based on its infrared spectrum and hydrolysis to  $\text{HClO}_4$ . Comparison of the infrared spectrum of this material and that of other covalent perchlorates revealed a dissimilarity but a spectrum of  $\text{Cl}_2\text{O}_6$  was not available for comparison. A sample of

$\text{Cl}_2\text{O}_6$  was prepared by uv irradiation of  $\text{ClO}_2$  (Ref. 16). Its infrared spectrum over the 2.5- to 25-micron region proved that the unidentified Cl-O material from the ClF reactions was  $\text{Cl}_2\text{O}_6$ . The volatility observed for the unknown Cl-O compound and that reported for  $\text{Cl}_2\text{O}_6$  are quite different. However, it was found in preparing the "authentic" sample of  $\text{Cl}_2\text{O}_6$  that its volatility and that of the ClF condensation reaction product were comparable and thus the reported vapor pressure data for  $\text{Cl}_2\text{O}_6$  are in error.

Reactions of  $\text{NO}_2\text{ClO}_4$  and  $\text{HClO}_4$  (72 percent) with ClF were also employed in the attempted preparation of  $\text{ClOClO}_3$ . The  $\text{NO}_2\text{ClO}_4$  proved to be relatively unreactive but did give very small amounts of a mixture of known Cl-O and FCl-O compounds including  $\text{Cl}_2\text{O}_6$  but no new material. The reaction of ClF and  $\text{HClO}_4$  was readily accomplished but here also the only observed products were mixtures of known chlorine-oxygen compounds. Thus, none of the attempted reactions gave any evidence for the formation of the desired  $\text{ClOClO}_3$  and efforts directed toward its synthesis were terminated.

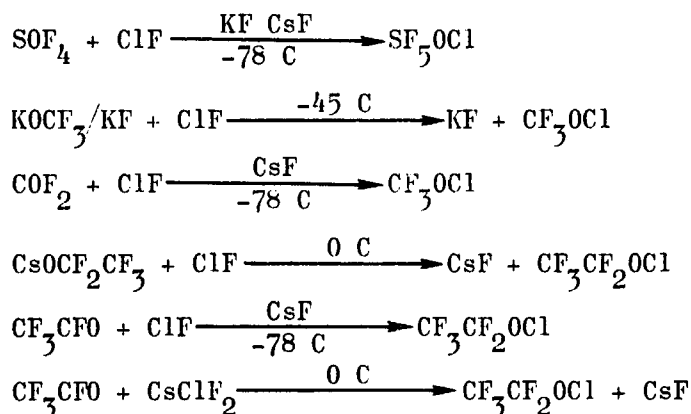
#### Preparation of Hypochlorites

Examples of the formation of both inorganic and organic hypofluorites have been reported recently (Ref. 17 and 18). The best technique for the synthesis of these compounds involves fluorination of a central atom-oxygen double bond in the presence of CsF at low temperature. For example:

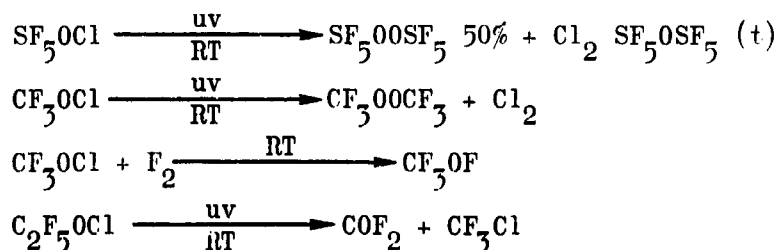


This Lewis base catalysis of the oxidation of  $\text{M}=\text{O}$  groups has now been applied to chlorofluorination reactions and has resulted in the preparation of some

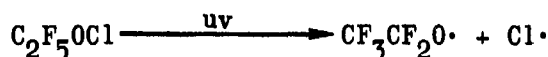
perfluorohypochlorites, a class of compounds previously unknown. The preparations have been conducted at temperatures down to  $-78^{\circ}\text{C}$  and have been found to rapidly produce hypochlorites in high yields. Some typical syntheses are summarized in the following reactions.

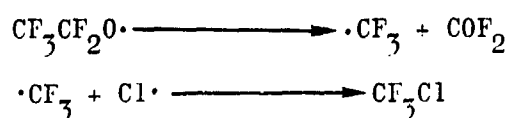


The identity of the product hypochlorites as such is based on the material balance observed in the syntheses and the vapor density of the products ( $\text{SF}_5\text{OCl}$ , calculated 178.5 gm/mole, found 177 gm/mole;  $\text{CF}_3\text{OCl}$ , calculated 120 gm/mole, found 110 gm/mole;  $\text{C}_2\text{F}_5\text{OCl}$ , calculated 170 gm/mole, found 164 gm/mole). In addition the infrared spectra of the products are similar to those of the corresponding known hypofluorites (Ref. 19) but lack any  $-\text{OF}$  absorptions. Finally, proof of the structure of the compounds was sought through derivative formation. Typical reactions obtained are:



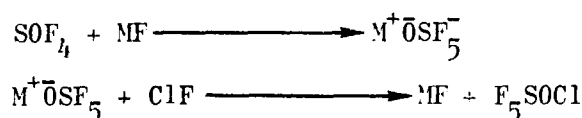
These reactions were nearly quantitative in the case of the perfluoroalkyl hypochlorites. The products observed in the photolysis of  $\text{C}_2\text{F}_5\text{OCl}$  probably arose in the following manner:





The three hypochlorites prepared are of variable stability in metal-Teflon systems at ambient temperature. The observed relative thermal stabilities are  $\text{SF}_5\text{OCl} < \text{C}_2\text{F}_5\text{OCl} < \text{CF}_3\text{OCl}$ . Decomposition occurs through disproportionation to the precursors, ClF and M=O. Further characterizing data will be obtained for these compounds.

The mechanism by which these compounds are formed is probably the same as that postulated for the catalytic fluorination reactions. For example:

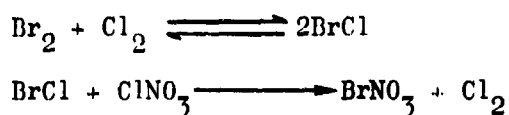


Only in the case of thionyl tetrafluoride has the necessity of MF in the reaction been shown as yet. Thus, no reaction was found for ClF and  $\text{SOF}_4$  in the absence of an alkali metal fluoride.

#### PREPARATION AND FLUORINATION OF BROMINE NITRATE

The fluorination of chlorine nitrate to give  $\text{ClF}_3\text{O}$  (Ref. 14) suggests that the analogous reaction of bromine nitrate might lead to  $\text{BrF}_3\text{O}$  or  $\text{BrF}_5\text{O}$ . Previous efforts (Ref. 1) in this area were hampered by the poor purity of the available  $\text{BrNO}_3$ . An improved synthetic method has now been devised which produces good purity material although it does so slowly.

The synthesis of  $\text{BrNO}_3$  has been accomplished through the in situ formation of BrCl from the elements, followed by reaction with  $\text{ClNO}_3$ .



The second step of this preparative scheme has been reported (Ref. 20) but previous attempts (Ref. 14) to utilize it were unsuccessful. Reaction of  $\text{Br}_2$ ,  $\text{Cl}_2$ , and  $\text{ClNO}_3$  in approximately 1:5:5 molar ratio in glass ampoules at  $-30$  to  $0^\circ\text{C}$  resulted in the formation of  $\text{BrNO}_3$ . The reaction has been carried out in the dark to minimize any possible photochemical decomposition. The product was obtained by fractional condensation at  $-64^\circ\text{C}$  and the only impurity was a small amount of  $\text{HNO}_3$ . The principal problem encountered with this method was that the reaction is quite slow at  $-30^\circ\text{C}$  while at  $0^\circ\text{C}$  some noncondensable gases are formed, probably due to decomposition of the desired product. Approximately 20 percent yield has been obtained in 1 week at  $-20^\circ\text{C}$ .

Bromine nitrate is pale yellow as a solid and melts at  $-31^\circ\text{C}$  to a golden liquid. The vapor pressure-temperature relationship for  $-25$  to  $10^\circ\text{C}$  is described by the equation  $\log p_{\text{mm}} = 9.6905 - 2254.5/T$ . The derived heat of vaporization is 10.3 kcal/mole. The principal infrared absorptions for  $\text{BrNO}_3$  are listed in Table 4.

TABLE 4

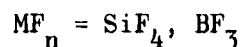
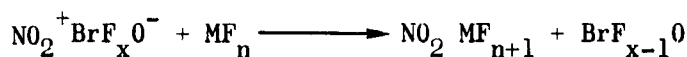
INFRARED SPECTRUM OF  $\text{BrNO}_3$ \*

Frequency, $\text{cm}^{-1}$	Relative Intensity	Frequency, $\text{cm}^{-1}$	Relative Intensity
3390	vw		
2970	w	955	w
2550	vw	800	vs
1700	vs	735	w
1440	vw	722	w
1280	vs	645	vw
1205	vw	555	vw
1110	w	450 pqr	vw

\*Spectrum taken on Perkin Elmer Models 137 and 337 spectrophotometers.

Fluorination of  $\text{BrNO}_3$  at  $-30^\circ\text{C}$  resulted in conversion to  $\text{BrF}_5$  and  $\text{FNO}_2$  only. Fluorination at ambient temperature or by slow warming from  $-78^\circ\text{C}$  to ambient temperature also gave  $\text{BrF}_5$  and  $\text{FNO}_2$  but in addition resulted in the formation of small amounts of a white solid, stable at room temperature. Infrared spectra showed this solid to be the same as that obtained previously (Ref. 1) by fluorinating impure  $\text{BrNO}_3$ . However, now that good purity  $\text{BrNO}_3$  has been successfully fluorinated, it has been found that the yields of free  $\text{FNO}_2$  and  $\text{BF}_3$  accounts for better than 95 percent of the starting Br and  $\text{NO}_2$  leaving very little as the complexed solid. The freedom from metal fluoride and other contaminants facilitated the obtaining of an infrared spectrum of the neat solid. This spectrum contained only the previously observed  $\text{NO}_2^+$  band ( $2385\text{ cm}^{-1}$ ) and a broad band (centered at  $575\text{ cm}^{-1}$ ) due to Br-F absorptions. No indication was found of an absorption due to a Br=O group as would be expected if the solid is the desired  $\text{NO}_2^+\text{BrF}_x\text{O}^-$  complex.

Chemical displacement of the Br-F function from this complex was attempted with Lewis acids.



No reaction was obtained between  $\text{SiF}_4$  and the complex at ambient temperature. Similar conditions when utilizing  $\text{BF}_3$  produced a slow reaction. After 2 days a small amount of  $\text{BF}_3$  was consumed but the only volatile material observed other than unreacted  $\text{BF}_3$  was  $\text{Br}_2$ . No noncondensable gases were formed. The solid left after this reaction was a mixture of  $\text{NO}_2\text{BF}_4$  and the original complex.

The observation of  $\text{Br}_2$  as a displacement product is indicative of an unstable Br-F species. The absence of noncondensables and the infrared spectrum of the

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complex indicate the absence of oxygen in the compound. The most readily apparent unstable bromine fluoride is BrF which exists only in the following equilibrium (Ref. 21):



If the observed Br<sub>2</sub> does arise from BrF, the coproduct BrF<sub>3</sub> would not have been observed due to the small quantities involved and its low vapor pressure.

Although no solid complexes of BrF have been reported, it is not unreasonable that the unknown complex, NO<sub>2</sub>BrF<sub>2</sub>, could be identical to the complex obtained in the BrNO<sub>3</sub> fluorination. To examine this possibility, a limited effort will be conducted to form NO<sub>2</sub>BrF<sub>2</sub>. This should be readily accomplished via FNO<sub>2</sub>, Br<sub>2</sub>, and F<sub>2</sub> if NO<sub>2</sub>BrF<sub>2</sub> is a stable solid. Additional fluorinations of BrNO<sub>3</sub> with F<sub>2</sub> as a route to BrF<sub>x</sub>O materials do not appear warranted due to the overwhelming cleavage at the Br-O bond rather than the O-NO<sub>2</sub> bond. Final attempts at effecting the desired bond breaking and fluorination will utilize ClF<sub>5</sub> as a fluorine source.

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## EXPERIMENTAL

## ULTRAVIOLET IRRADIATION

Cell and Fractionation System

A specially designed ultraviolet reactor was connected to the system and consisted of a stainless-steel body and a 4-inch-diameter ultraviolet-grade sapphire window. The cell temperature was automatically controlled by a circulating methanol cooling system to within 3 C of the desired temperature and within a range of -60 C to ambient temperature. The cell apparatus was modified so that a new ultraviolet lamp could be used. This modification consisted of a metal housing above the cell window to hold the new lamp and a system to supply dry nitrogen which can be blown continuously across the cell window to prevent "frosting" during low-temperature reactions. The new lamp provided a greatly increased amount of irradiation; however, it also increased the amount of heat generated and it was necessary to cool the cell housing with a large fan.

Ultraviolet Source

Work was conducted with a Hanovia lamp No. 679-A-36 (power input 450 watts). The spectral energy distribution of radiated Hg lines include (wavelength in angstroms, and watts): 2967, 4.3; 2652, 4.0; 2537, 5.8; 2482, 2.3; 2380, 2.3; 2360, 2.3; 2224, 3.7.

Materials

The  $\text{FClO}_2$  was prepared by the reaction of  $\text{ClF}_3$  and  $\text{KClO}_3$ . Purification of  $\text{FClO}_2$  was carried out by pumping off the  $\text{Cl}_2$  impurity while holding

the  $\text{FClO}_2$  at  $-78^\circ\text{C}$ . The chromatographic purity of the colorless liquid was better than 99.9 percent. The  $\text{FClO}_3$  was purchased from Pennsalt. The  $\text{ClF}_5$  prepared at Rocketdyne, had a purity of 99+ percent. Other materials were prepared by standard techniques.

## CHLORINE MONOFLUORIDE REACTIONS

### Synthesis of $\text{Cl}_2\text{F}^+\text{AsF}_6^-$

All reactions were carried out in a stainless-steel vacuum line equipped with Teflon FEP U-traps.

In a typical experiment, 96.7 mmoles of  $\text{ClF}$  (prepared in this laboratory and purified by fractional condensation) and 24.2 mmoles of  $\text{AsF}_5$  (obtained from Ozark-Mahoning and purified by fractional condensation) were combined at  $-196^\circ\text{C}$  in a U-trap. The mixture was allowed to warm slowly until melting and reaction occurred. When the pressure inside the trap reached 760 mm the mixture was cooled again to  $-196^\circ\text{C}$ . This procedure was repeated several times until completion of the reaction. The content of the trap was maintained at  $-78^\circ\text{C}$  and all volatiles were pumped off and condensed at  $-196^\circ\text{C}$ . The content of the  $-196^\circ\text{C}$  trap consisted of 48.8 mmoles of  $\text{ClF}$ . The observed vapor pressure-temperature data for the complex are presented in Table 5.

### Synthesis of $\text{Cl}_2\text{F}^+\text{BF}_4^-$

The synthesis of  $\text{Cl}_2\text{F}^+\text{BF}_4^-$  was similar to that of  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  except that the U-trap containing the solid complex was maintained at  $-126^\circ\text{C}$  when the excess  $\text{ClF}$  was removed in vacuo.

TABLE 5

VAPOR PRESSURE-TEMPERATURE DATA FOR  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$ 

Pressure, mm Hg	Temperature, C
1.7	-63.76
6.0	-54.30
16.5	-45.45
68.5	-30.11
120	-24.77
209	-11.15

Low-Temperature Infrared Spectra

The technique used to obtain the low-temperature infrared data is described in Ref. 22.

Displacement Reaction of  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  With  $\text{NO}_2\text{F}$ 

Nitryl fluoride (2.75 mmoles, prepared in this laboratory and purified by fractional condensation) was combined with a large excess of solid  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  at -196 C. The temperature of the trap containing the mixture was cycled between -196 C and a temperature where the pressure inside the trap reached 1 atmosphere until the reaction was complete. The trap was maintained at -78 C and all volatiles were removed to a -196 C trap. The content of the -196 C trap was shown to consist of 5.33 mmoles of essentially pure ClF.

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## Reactions of ClF and Perchlorates

Samples of the substrate perchlorates were transferred to prepassivated 10- or 30-milliliter stainless-steel bombs in a nitrogen-filled dry box. The solid perchlorates were commercial dry, powdered, white solids ( $\text{NaClO}_4$ ,  $\text{CsClO}_4$ , and  $\text{NO}_2\text{ClO}_4$ ). Once the reactors were closed and re-evacuated, freshly fractionated ClF was condensed in at  $-196^\circ\text{C}$ . The reactors were then changed to the desired reaction temperature ( $-78$ ,  $-45$ , or  $0^\circ\text{C}$ ) and left for up to 2 weeks. On completion of the reaction, the gaseous products were separated by fractional condensation at  $-78$ ,  $-112$ ,  $-142$ , and  $-196^\circ\text{C}$ . Generally 80+ percent of the ClF was recovered (excesses of  $\text{MClO}_4$  were used) and the remaining products were mixtures of  $\text{FClO}_2$ ,  $\text{FClO}_3$ ,  $\text{Cl}_2$ , and variable amounts of  $\text{Cl}_2\text{O}_6$ . No unidentified volatile species were found.

## Synthesis of Hypochlorites

Method A. An alkali metal salt ( $\text{MOR}_f$ ;  $\text{M}=\text{K}, \text{Cs}$  and  $-\text{OR}_f=\text{OCF}_3$  or  $\text{OC}_2\text{F}_5$ ) was placed in a prepassivated stainless-steel reactor. Chlorine monofluoride was condensed into the reactors at  $-196^\circ\text{C}$  and the closed bomb was allowed to stand at temperatures between  $-78$  and  $0^\circ\text{C}$  for time periods up to several weeks. Fractionation of the volatile products after even short time periods showed the reaction to be complete giving  $\text{R}_f\text{OCl}$  as the product and any excess ClF. Purification by fractional condensation was effected and both perfluoromethyl hypochlorite and perfluoroethyl hypochlorite were identified by vapor density measurements and infrared spectra.

Method B. A prepassivated, stainless-steel cylinder was loaded with  $\text{MF}(\text{KF}$  or  $\text{CsF})$  in a dry box. After evacuation, measured amounts of an  $\text{M}=\text{O}$  compound ( $\text{M}=\text{O}$  is  $\text{COF}_2$ ,  $\text{CF}_3\text{CFO}$ , or  $\text{SOF}_4$ ) were condensed in at  $-196^\circ\text{C}$  followed by a molar excess of freshly fractionated ClF. The reactor was then warmed to  $-78^\circ\text{C}$  for 1 hour or more. Subsequent vacuum fractionation

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of the contents showed that conversion of  $M=0$  to the corresponding hypochlorite ( $CF_3OCl$ ,  $C_2F_5OCl$ ,  $SF_5OCl$ ) had occurred in high yield. Proof of the composition of  $SF_5OCl$  was accomplished through vapor density measurement, synthetic material balance, and infrared spectroscopy just as had been accomplished earlier with the  $RF_3OCl$  compounds. The conversion of  $SOF_4$  to  $SF_5OCl$  was shown to be slower with  $KF$  than with  $CsF$  and also it was shown that  $ClF$  and  $SOF_4$  do not form  $SF_5OCl$  in the absence of  $KF$  or  $CsF$  under comparable conditions.

Method C. A sample of  $CsClF_2$  solid contained in a 10-milliliter stainless-steel reactor was treated with  $CF_3CFO$  at approximately 0 C for 15 minutes. Fractionation of the gaseous materials at that time showed 25 percent of the  $CF_3CFO$  had been converted to  $C_2F_5OCl$ . Returning the gases over the  $CsClF_2$  at -45 C for several hours resulted in nearly complete conversion to  $C_2F_5OCl$ .

#### Reactions of Hypochlorites

Chemical characterization of these hypochlorites was carried out to substantiate the formulations.

Photochemical decomposition by uv irradiation (100-watt Hanovia utility lamp) was accomplished at ambient temperature. Irradiations were conducted using Pyrex containers and 1- to 2-hour reaction times. In the case of  $CF_3OCl$ , the reaction completely consumed the hypochlorite and formed  $CF_3OOCF_3$  and  $Cl_2$  in very high yield. In the case of  $C_2F_5OCl$ , the product volume again was almost precisely double that of the starting volume but infrared examination showed the products to be a 1:1 mixture of  $COF_2$  and  $CF_3Cl$ . The photolysis of  $SF_5OCl$  resulted in approximately a 50 percent yield of  $SF_5OOSF_5$  with a trace of  $SF_5OSF_5$ . No  $SF_5OCl$  was recovered as it had decomposed through thermal or uv excitation or both to give  $SOF_4$  and  $ClF$  (observed as  $Cl_2$ ,  $SiF_4$ ).

Fluorination of  $\text{CF}_3\text{OCl}$ . The conversion of  $\text{CF}_3\text{OCl}$  to the known  $\text{CF}_3\text{OF}$  occurred in minutes at ambient temperature or below through reaction with excess  $\text{F}_2$ . Only a small amount of  $\text{CF}_3\text{OCl}$  was recovered and the only other C-F product in addition to  $\text{CF}_3\text{OF}$  was a trace of  $\text{COF}_2$ .

#### BROMINE NITRATE PREPARATION AND FLUORINATION

A typical preparation of  $\text{BrNO}_3$  has employed  $\text{Br}_2$  (100 cc),  $\text{Cl}_2$  (400 to 500 cc), and  $\text{ClNO}_3$  (400 to 500 cc) in a 30-milliliter glass ampoule. The closed ampoule was maintained at a constant temperature (-30, -21 or 0 C) for several days. To a degree, the course of the reaction could be followed by observing the color of the solution. Originally, this was very dark red but as  $\text{Br}_2$  was converted to  $\text{BrCl}$  and  $\text{BrNO}_3$  it gradually changed to cherry red. At -30 C, the reaction is very slow while at 0 C some noncondensable by-products are formed. The reactors were kept in the dark to limit any possible photochemical decomposition. Bromine nitrate was purified by removing most of the  $\text{Cl}_2$ ,  $\text{ClNO}_3$ , and  $\text{BrCl}$  at -78 C. After this was accomplished, a final fractionation through -45 and -65 C traps yielded  $\text{BrNO}_3$  whose infrared spectrum showed only negligible  $\text{HNO}_3$  contamination. Vapor pressure-temperature readings for the -25 to 10 C range are presented in Table 6. A typical infrared spectrum of  $\text{BrNO}_3$  is shown in Fig. 3.

TABLE 6  
VAPOR PRESSURE-TEMPERATURE DATA FOR  $\text{BrNO}_3$

Pressure, mm Hg	Temperature, C
4	-24.9
7	-18.5
10	-13.9
21	-3.5
29	+0.8
33	+2.7
44	+7.0

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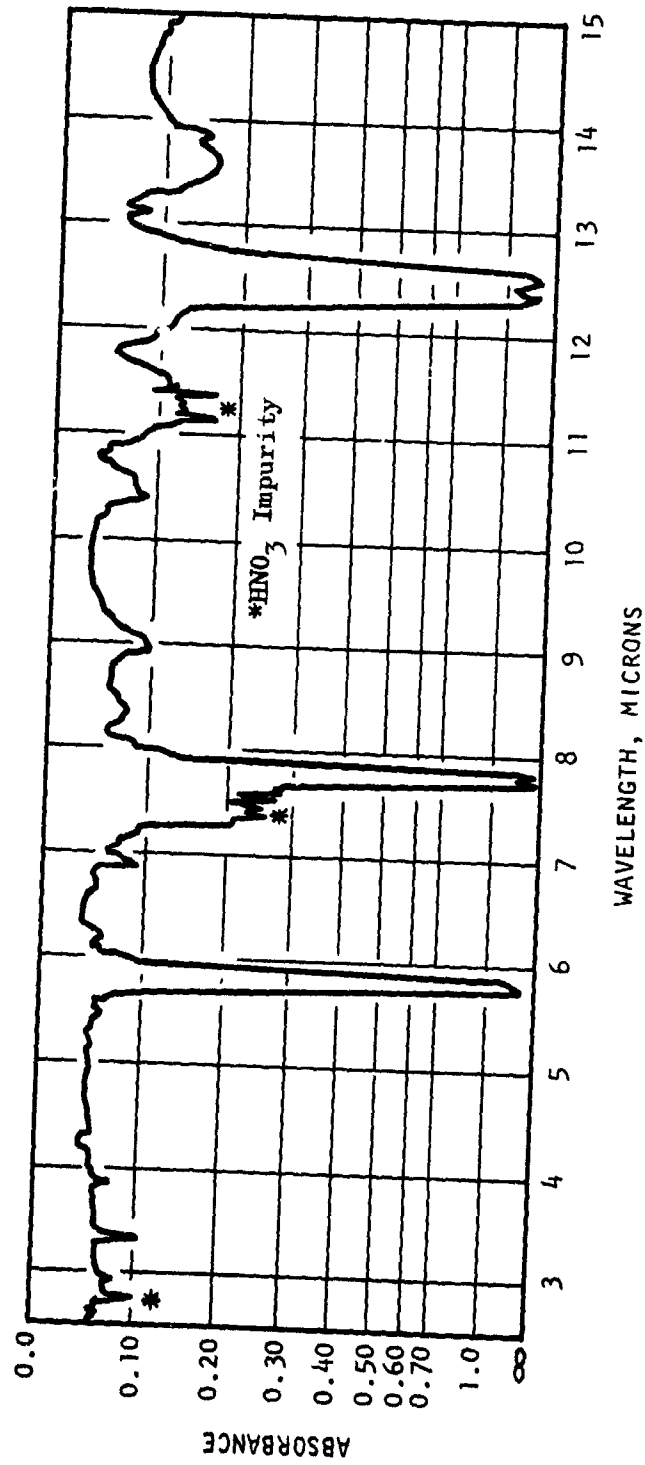


Figure 3. Bromine Nitrate Infrared Spectrum (5 cm path/20 mm Pressure)

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Measured samples of  $\text{BrNO}_3$  were condensed into 30-milliliter stainless-steel cylinders at  $-196^\circ\text{C}$  followed by excess  $\text{F}_2$ . The reaction was allowed to proceed at a constant temperature ( $-30^\circ\text{C}$ ) or by slow warming to ambient temperature for overnight or longer. After removal of the excess  $\text{F}_2$  at  $-196^\circ\text{C}$ , the remaining volatile products were fractionated through traps cooled to  $-78^\circ$ ,  $-142^\circ$ , and  $-196^\circ\text{C}$  as the reactor warmed. These materials were found to be pure  $\text{FNO}_2$  and  $\text{BrF}_5$  and accounted for 95+ percent of the charged  $\text{BrNO}_3$ . Examination of the reaction cylinders in the dry box showed residual solids (tan or white in color) whose infrared spectrum, and hydrolytic and thermal decomposition during this and previous reporting periods (Ref. 1) have shown to be an  $\text{NO}_2^+$  complex of an undetermined bromine fluoride. Chemical displacement of the anionic bromine fluoride species from this complex was attempted with  $\text{SiF}_4$  and  $\text{BF}_3$ . The former did not react and the latter gave only slight reaction but liberated  $\text{Br}_2$  only as an observed volatile product. The solid was shown by infrared spectroscopy to have been at least partially converted to  $\text{NO}_2\text{BF}_4$ .

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13. ABSTRACT  Ultraviolet activated fluorinations of chlorine oxyfluorides at low temperatures to produce Florox were continued. The involvement of elemental $\text{Cl}_2$ and $\text{O}_2$ in the Florox forming process was deduced and was verified experimentally by the preparation of Florox from $\text{Cl}_2$ , $\text{F}_2$ , and $\text{O}_2$ . The chlorofluoro chloronium (III) cation, $\text{Cl}_2\text{F}^+$ , a new oxidizing species, has been prepared in the form of its $\text{AsF}_6^-$ and $\text{BF}_4^-$ salts. The white crystalline $\text{Cl}_2\text{F AsF}_6$ complex is stable at $-78^\circ\text{C}$ and is completely dissociated in the gas phase at $25^\circ\text{C}$ . Low-temperature infrared measurements on both salts prove the ionic nature of the solids and indicate that $\text{Cl}_2\text{F}^+$ has a bent structure (symmetry $\text{C}_s$ ) with chlorine as the central atom. The $\text{Cl}_2\text{F}^+$ cation is the first example of a catenated polyhalogen cation. The utility of $\text{ClF}$ as a chlorofluorinating agent was demonstrated in the preparation of some new covalent hypochlorites, $\text{R}_2\text{OCl}$ . These syntheses are catalyzed by alkali metal fluorides but may also be affected by reaction of preformed complexes. High-purity bromine nitrate has been prepared by the reaction of $\text{Br}_2$ , $\text{Cl}_2$ , and $\text{ClNO}_2$ at $-30$ to $0^\circ\text{C}$ . Solid $\text{BrNO}_2$ is pale yellow and melts to a golden colored liquid at $-31^\circ\text{C}$ . The vapor pressure-temperature equation for $-25$ to $10^\circ\text{C}$ is $\log p_{\text{mm}} = 9.6905 - 2254.5/T$ . Fluorination of $\text{BrNO}_2$ has shown that $\text{FNO}_2$ and $\text{BrF}_5$ are the principal products (95+ percent yield). (C)			

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